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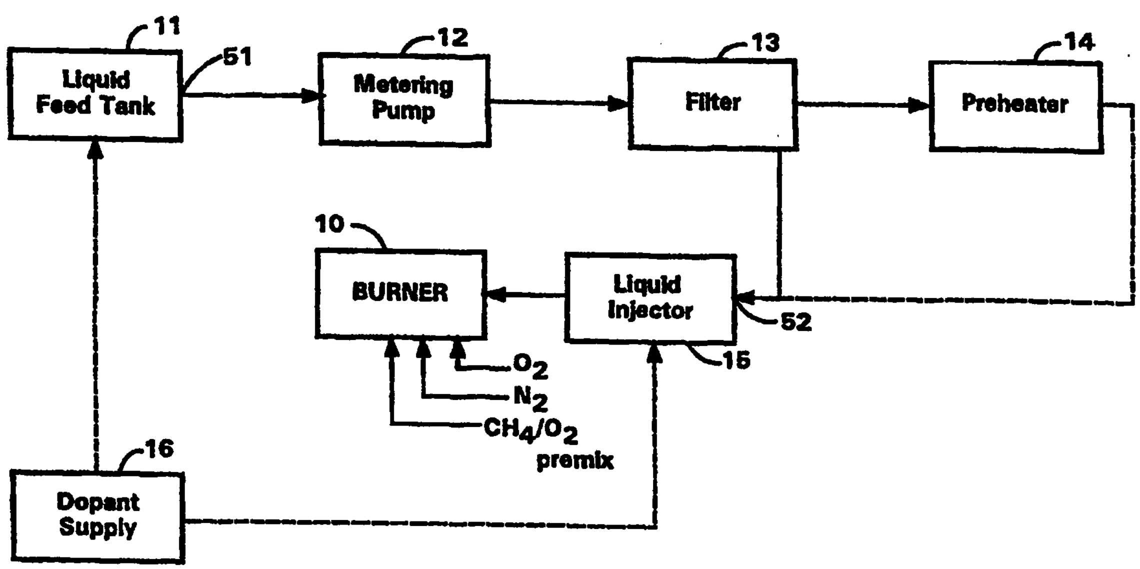

(57) Abstract

The present invention is directed to a method for making silica. A liquid siloxane–containing feedstock capable of being converted by thermal oxidative decomposition to SiO_2 is provied and introduced directly into the flame of a combustion burner, which converts the compound to silica, thereby forming finely divided amorphous soot. The soot is vaporized at the conversion and/or deposition site where the liquid is converted into silica by atomizing the liquid with a stream of oxygen gas, or a mixture of oxygen gas and other gas, such as nitrogen. The amorphous soot is deposited on a receptor surface where, either substantially simultaneously with or subsequently to its deposition, the soot is consolidated into a body of fused silica glass, such as an optical fiber preform.

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METHOD FOR FORMING SILICA BY COMBUSTION OF LIQUID REACTANTS USING OXYGEN

This application is a continuation-in-part of U.S. Patent Application Serial No. 08/767,653, filed on December 17, 1996, the content of which is relied upon and incorporated by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to the formation of silica and silica preforms and, more particularly, to a method and apparatus for forming silica and silica preforms from liquid silicon-containing compounds.

BACKGROUND OF THE INVENTION

Various processes are known in the art that involve the production of metal oxides from vaporous reactants. Such processes require a feedstock solution, a means of generating and transporting vapors of the feedstock solution (hereafter called vaporous reactants) and an oxidant to a conversion reaction site, and a means of catalyzing oxidation and combustion coincidentally to produce finely divided, spherical aggregates, called soot. This soot can be collected on any deposition receptor in

any number of ways ranging from a collection chamber to a rotating mandrel. It may be simultaneously or subsequently heat treated to form a non-porous, transparent, high purity glass article. This process is usually carried out with specialized equipment having a unique arrangement of nozzles and burners.

Much of the initial research that led to the development of such processes focused on the production of bulk silica. Selection of the appropriate feedstock was an important aspect of that work. Consequently, it was at that time determined that a material capable of generating a vapor pressure of 200-300 millimeters of mercury (mm Hg) at temperatures below 100°C would be useful for making such bulk silica. The high vapor pressure of silicon tetrachloride ($SiCl_4$) suggested its usefulness as a convenient vapor source for soot generation and launched the discovery and use of a series of similar chloride-based feedstocks. This factor, more than any other, is responsible for the presently accepted use of $SiCl_4$, $GeCl_4$, $POCl_3$, and BCl_3 as vapor sources, even though these materials have certain chemically undesirable properties.

Although use of halide-free silicon compounds as feedstocks for fused silica glass production, as described in U.S. Patent Nos. 5,043,002 and 5,152,819, avoids the formation of HCl, some problems remain, particularly when the glass is intended for the formation of optical waveguides and high purity silica soot. Applicants have found that, in the course of delivering a vaporized polyalkylsiloxane feedstock to the burner, high molecular weight species can be deposited as a gel in the line carrying the vaporous reactants to the burner or within the burner itself. This leads to a reduction in the deposition rate of the soot preform that is subsequently consolidated to a blank from which an optical waveguide

fiber is drawn. It also leads to imperfections in the blank that will produce defective or unusable optical waveguide fiber from the affected portions of the blank.

In copending Application Serial No. 08/767,653, it was disclosed that the clustered defects could be reduced by delivering a liquid siloxane feedstock to a conversion site, atomizing the feedstock at the conversion site, and converting the atomized feedstock at the conversion site into silica. One way to atomize the feedstock at the conversion site involves pneumatically or airblast atomizing the liquid siloxane feedstock at the conversion site with a delivery gas such as an inert gas. By "pneumatic" or "airblast" atomizing, we do not mean that air must be used as the atomizing gas, and the gas can also be an inert gas such as argon, nitrogen, or helium, a combustible gas such as methane, oxygen, or a mixture of these gases.

Even though atomizing the liquid feedstock reduces clustered defects, such a liquid delivery system presents several challenges. For example, increasing the delivery gas velocity desirably produces smaller liquid droplets, which are more readily vaporized and burned in the burner flame. Smaller droplets are desirable because larger droplets cause wart-like defects ("warts") on the surface of the soot blank. In addition, smaller droplets can be more easily focused with the surrounding gases to produce a more focused deposition stream. On the other hand, increasing atomizing gas velocity adds turbulence to the burner flame, which can reduce soot capture rate and appears to be one cause of a physical soot defect known as "lizard skin." Lizard skin is a term for a rough soot blank surface.

Accordingly, it would be desirable to provide a method in which a liquid delivery system could produce a

focused deposition stream containing small droplets without a high gas velocity, and in which there is low burner flame turbulence.

SUMMARY OF THE INVENTION

The present invention is directed to a method for making silica. In one embodiment, a liquid, preferably halide-free, silicon-containing compound capable of being converted by thermal oxidative decomposition to SiO_2 is provided and introduced directly into the flame of a combustion burner, thereby forming finely divided amorphous soot. The amorphous soot may be deposited on a receptor surface where, either substantially simultaneously with or subsequently to its deposition, the soot can be consolidated into a body of fused silica glass. The body of fused silica glass can then be either used to make products directly from the fused body, or the fused body can be further treated, e.g., by forming a an optical waveguide such as drawing to make optical waveguide fiber further see, e.g., the end-uses described in the U.S. Patent Application No. 08/574,961 entitled "Method for Purifying Polyalkylsiloxanes and the Resulting Products", the contents of which are hereby incorporated by reference.

The invention further comprises an apparatus for forming silica from liquid, preferably halide-free, silicon-containing reactants that comprises: a combustion burner which, in operation, generates a conversion site flame; an injector for supplying a liquid silicon-containing compound to the flame to convert the compound by thermal oxidative decomposition to a finely divided amorphous soot; and a receptor surface positioned with

respect to said combustion burner to permit deposition of the soot on the receptor surface.

The applicants have now discovered that the above-described problem is inhibited by delivering the siloxane feedstock in the liquid form to the conversion site during the silica manufacturing process. By delivering the siloxane feedstock as a liquid instead of as a vapor, gelling of the siloxane feedstock is prevented in that exposure of the siloxane feedstock to the high temperature environments of a vaporizer and vapor delivery system are avoided. This improves the yield and quality of the silica produced and also reduces the maintenance requirements of the production system.

Thus, the invention provides a method of inhibiting the gelling of a siloxane feedstock in the silica manufacturing process by delivering the siloxane feedstock to the conversion site in a liquid form. Since the hot environments of the vaporizer and vapor delivery system, which promote the formation of troublesome gels, are avoided, the silica manufacturing process is improved. The siloxane feedstock is delivered to the conversion site as a liquid and does not vaporize until just prior to or simultaneous with being converted into amorphous silica soot. The amorphous silica soot is then deposited on a receptor surface. Either substantially simultaneously with or subsequently to its deposition, the soot can be consolidated into a body of fused silica glass, from which e.g., an optical waveguide fiber can be formed by drawing.

Another aspect of the invention further comprises a silica manufacturing apparatus which includes a siloxane liquid feedstock tank for containing the siloxane liquid feedstock and a siloxane liquid feedstock transporting conduit for delivering the siloxane liquid feedstock to an injector which injects the liquid feedstock into the

conversion site where it is decomposed in a combustion burner flame to form a finely divided amorphous silica soot which is deposited on a receptor surface.

The body of fused silica glass can be doped with an oxide dopant wherein, in addition to the liquid siloxane feedstock, a dopant compound that is capable of being converted by oxidation or flame hydrolysis to a member of the group consisting of P_2O_5 and metal oxide having a metal component selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, VA, and the rare earth series of the Periodic Table of Elements is introduced into the flame of the burner. The oxide-doped fused silica glass so obtained can be, e.g., drawn into an optical waveguide fiber.

In still another aspect of the present invention, applicants have discovered that by pneumatically atomizing the siloxane liquid feedstock at the conversion site with a stream of flowing oxygen, the defects on the blank are greatly reduced. Thus, by using oxygen as the delivery gas in a pneumatic atomizer, much smoother and better quality fused silica blanks can be made.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram of a reactant delivery system in accordance with the present invention.

FIG. 2 is a schematic representation of liquid reactant provided to the flame of a burner from a syringe in accordance with the present invention.

FIG. 3 is a schematic representation of liquid reactant particles being provided to the flame of a burner from a transducer in accordance with the present invention.

FIG. 4 is a schematic representation of an atomizer incorporated into the structure of a burner in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 schematically depicts a system for delivering liquid feedstock and, optionally, dopant-providing compounds to burner 10. A liquid siloxane feedstock such as a polymethylcyclosiloxane is stored in feedstock tank 11. Feedstock tank 11 is connected to liquid feedstock injector 15 at the reactant introduction site via a liquid feedstock transporting conduit system that can, if desired, include metering pump 12, optional filter 13, and preheater 14. Said liquid feedstock transporting conduit has a first terminal end 51 and a second terminal end 52. The siloxane feedstock liquid from tank 11 is transferred through the liquid feedstock transporting conduit by pump 12 through filter 13 to optional preheater 14. The liquid delivered through filter 13 is under sufficient pressure to substantially prevent and inhibit its volatilization in preheater 14, which is optionally employed to warm the liquid reactant prior to its introduction into burner 10 and avoids the high temperatures of a vaporizer which normally promote gel formation. The burner preferably is conventionally provided with inner shield gas, outer shield gas, and a mixture of methane and oxygen for the flame, as described, for example, in U.S. Patent No. 4,165,223 to D.R. Powers, which is hereby incorporated by reference.

The liquid reactant is conveyed from optional filter 13 or optional preheater 14 through second terminal end 52 to liquid injector 15, which delivers the liquid to burner

10. Injector 15 comprises a device for delivering the liquid reactant, either as a liquid stream or as atomized liquid particles, directly into the flame of burner 10. We generally refer in the discussion to the reactant as being in "liquid" form. What we mean by that expression is that the reactant is in a substantially liquid state. Some small portion of the reactant may be in vapor form, particularly where preheater 14 is employed, or where a nitrogen blanket over the liquid is employed. A small portion of the reactant can be in vapor form as delivered to the combustion site without adversely affecting the operation of the invention.

Liquid injector 15 can comprise, for example, a syringe provided with a fine needle, by which a liquid stream can be injected at high velocity into the burner flame. Although a syringe can be used on a small scale, commercial operations will require a reasonable large scale equivalent, e.g., an atomizer.

Several types of atomizing means capable of forming very small particles of liquid are known in the atomization art as disclosed in Atomization and Sprays, by Arthur H. Lefebure, Hemisphere Publishing Co., 1989, which is incorporated herein by reference. Atomizers can be operated by various energy sources such as liquid, gas, mechanical, electrical and vibrational, and may be categorized as, for example, jet, swirl, jet-swirl, pneumatic, rotary, acoustic, ultrasonic, and electrostatic. Preferably, a jet atomizer is used; even more preferably, the jet atomizer is a swirl-jet atomizer, which swirls the liquid and then, as atomizers generally do, squirts the liquid at high velocity out of a small orifice. Various types of atomizers are discussed in Liquid Atomization, by L. Bayvel and Z. Orzechowski,

Taylor & Francis, (1993), which is hereby incorporated by reference.

Another preferred type is a pneumatic atomizer operated by nitrogen or air pressure. In particularly preferred embodiments, the atomizer can be incorporated into the structure of the combustion burner.

The atomized particles of the siloxane reactant compound are combusted in a burner fueled by, preferably, a combination of methane and oxygen. The atomized reactant particles can be conveyed from the atomizer to the burner flame by a carrier gas such as nitrogen, which is preferably the atomizing gas. More preferably, a mixture of nitrogen and oxygen is used as the atomizing gas. Most preferably, oxygen is used as the atomizing gas to reduce the formation of defects on the soot blank.

FIG. 2 schematically depicts an apparatus in accordance with the present invention, in which syringe 21 injects a liquid reactant stream 22 into conversion site flame 23 produced by burner 24. Thermal oxidative decomposition of the reactant produces finely divided amorphous soot 25, which is deposited on rotatable mandrel 26.

FIG. 3 is a schematic representation of another embodiment of the apparatus of the present invention, whereby atomizer 31 injects small liquid reactant particles 32 into flame 23 produced by burner 24. Combustion of the reactant yields soot 25, which is deposited on rotatable mandrel 26.

FIG. 4 is a cross-sectional view of a preferred embodiment of the apparatus of the present invention. Here, burner 40 incorporates within its structure atomizer 41, which injects very finely atomized liquid reactant particles into flame 23. As with the previously described

embodiments, amorphous soot 25 produced by combustion of the liquid reactant is collected on rotatable mandrel 26.

As shown in FIG. 4, burner 40 comprises a series of concentric channels surrounding atomizer 41. Liquid siloxane is delivered through atomizer 41. A stream of an inert gas such as nitrogen gas, a mixture of oxygen gas and nitrogen gas, or oxygen gas alone delivered through channel 43 atomizes the liquid feedstock by the kinetic energy of the flowing gas to create liquid projections 42 which are converted into soot reactant particles in burner flame 23. The area proximate to the burner face 53 and flame 23 thus acts as a conversion site for converting liquid projections 42 into soot reactant particles. Oxygen gas may be delivered to flame 23 through channels 45 and 46. An inert gas, such as nitrogen, argon or helium is delivered through channel 44 to inhibit reaction of the liquid feedstock and soot build-up on burner face 53. Applicants have found that when oxygen or a mixture of oxygen and inert gas is used as the atomizing gas, better results are obtained by delivering an inert gas through channel 44. A premix of oxygen and a fuel such as methane is conducted to the flame through outermost channel 47. A burner fitted with an atomizing injector, such as the embodiment depicted in FIG. 4, produces a wide soot stream, which achieves improved concentricity of the core and cladding regions of a subsequently formed optical waveguide fiber.

The most preferred burner 40 of the invention as shown in FIG. 4 is comprised of a pneumatic atomizer. With such a pneumatic atomizer, the liquid siloxane feedstock delivered through atomizer 41 is atomized by the kinetic energy of a flowing gas stream through inner most channel 43. High velocity gas is utilized in atomizing the feedstock. This produces atomized liquid projections

42 with a velocity in the range of 0.5 to 50.0 m/sec. The use of an inert gas such as N_2 gas is preferred with the pneumatic atomizer. Use of N_2 gas as the pneumatic gas helps to blanket the feedstock from the oxygen in the flame and prevents burner buildup.

To reduce the velocity of the atomizing gas and prevent surface defects on the soot blank, O_2 gas is the most preferred gas to be used with the pneumatic atomizer. It was previously believed that O_2 would not help to prevent combustion of the feedstock prior to full vaporization of the liquid feedstock. However, applicants have discovered that using oxygen as the atomizing gas allows better mixing of the siloxane with oxygen before conversion to soot. It is believed that use of this atomizing gas results in quicker heating of the liquid and helps provide the O_2 needed for the reaction. Therefore, the velocity of the oxygen atomizing gas can be significantly lowered, at least by about 50% of the velocity of nitrogen atomizing gas. This reduction in gas velocity consequently reduces burner flame turbulence and soot blank defects.

It was also observed that using a mixture of oxygen and nitrogen as the atomizing gas allowed for lower atomizing gas velocity and reduced blank defects. For example, a mixture of 75% oxygen gas and 25% nitrogen gas by volume as the atomizing gas enabled a significant reduction in atomizing gas velocity and a reduction in soot blank defects. However, compared to this example, using oxygen alone provided for a lower atomizing gas velocity.

With the use of the pneumatic atomizer in the invention, the high velocity blast gas is deployed in an effective manner to achieve a beneficial level of

atomization of the siloxane at the burner and in the flame.

In practicing the invention, even though it is preferred to have atomizer unit 41 as an integral part of the burner unit 40, it is possible to use a pneumatic atomizer which is spatially separated from the burner, as with atomizers 21 and 31 in FIG. 2 and FIG. 3.

The apparatus can also be provided with dopant supply tank 16, shown in FIG. 1, which contains a compound capable of being converted by oxidation or flame hydrolysis to P_2O_5 or to a metal oxide whose metallic component is selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the Periodic Table. These oxide dopants combine with the silica generated in the burner to provide doped silica glass, which can be subsequently formed into optical waveguide fibers.

The compound that provides the silica glass dopant can be provided to feed tank 11 from dopant supply 16 of FIG. 1. Alternatively, the dopant can be delivered from supply 16 to liquid injector 15 via a separate metering pump and optionally a filter (not shown) analogous to the delivery system used for the silicon-containing compound.

In accordance with the invention, the preferably halide-free, silicon-containing reactant compound preferably comprises a polyalkylsiloxane, for example, hexamethyldisiloxane. More preferably, the polyalkylsiloxane comprises a polymethylcyclosiloxane. Most preferably, the polymethylcyclosiloxane is selected from the group consisting of hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, and mixtures thereof.

As disclosed in copending U.S. Patent Application No. 08/574,961, the use of such siloxane feedstocks as octamethylcyclotetrasiloxane poses problems with the conventional silica manufacturing process in that the siloxane feedstock is prone to polymerize and form gels, which clog and impede the feedstock vaporizer and vaporized feedstock delivery system.

The following examples further illustrate the invention.

Example 1 - Soot Generation by Injection of Liquid Reactant into a Flame with a Syringe

A stream of liquid octamethylcyclotetrasiloxane (OMCTS) was injected into a burner flame of a lathe fitted with a glass rod using a syringe provided with a 0.01-inch diameter needle. The resulting porous soot particles containing SiO_2 were collected on the rotating one-inch diameter glass rod. This procedure demonstrates the feasibility of obtaining SiO_2 by combustion of the siloxane feedstock compound in liquid form.

Example 2 - Generation of Soot Using an Ultrasonic Transducer Atomizer as Injector

Liquid octamethylcyclotetrasiloxane (OMCTS) was delivered to a combustion burner via a Vibra-Cell® 20-khz ultrasonic transducer atomizer (available from Sonics & Materials, Inc., Danbury, CT) inserted down the centerline of the burner. The atomizer was surrounded by two inner rings of oxygen supply and an outer ring of premixed CH_4/O_2. The following flow rates were employed: octamethylcyclotetrasiloxane (OMCTS), 11 grams per minute; oxygen, 10 standard liters per minute (SLPM); premix, 10 SLPM CH_4 and 8.4 SLPM O_2.

Combustion was continued for about 10 minutes. A good deposit of SiO_2 soot was collected on the mandrel, further demonstrating the practicality of producing SiO_2 from a siloxane feedstock introduced as small liquid particles into the burner flame.

Example 3 - Soot Generation by an Atomizing Combustion Burner

An atomizing burner was constructed as depicted in FIG. 4. Various dimensions of atomizer 41 and the surrounding channels were tested, as follows:

inner diameter of atomizer 41: 0.007 to 0.015 inch
inner diameter of channel 43: 0.036 to 0.050 inch
outer diameter of channel 43: 0.048 to 0.063 inch

Using an atomizer 41 having an 0.015-inch inner diameter, particles of soot were generated from octamethylcyclotetrasiloxane (OMCTS) for 65 minutes. Flow rates were as follows:

Premix through channel 46: 10 SLPM CH_4 and 8 SLPM O_2.
O_2 through channels 44 and 45: 26 SLPM.
N_2 through channel 43: 5.6 SLPM.
Octamethylcyclotetrasiloxane (OMCTS) through atomizer 41: 6 milliliters per minute (ml/min) for first five minutes, then 10 ml/min for next 60 minutes.

The target or bait, a 1-inch diameter glass rod, was set to rotate between 1 and 5 rotations per second, traversing back and forth at about 15 meters per minute. The burner to bait receptor surface distance was about 6.5 inches.

Complete combustion of the reactant octamethylcyclotetrasiloxane (OMCTS) was achieved, and the target weight increased by 247 grams over the 65-minute deposition period (3.8 grams/minute). The soot was subsequently consolidated in a furnace, yielding glass that was clear and free of visible defects.

The invention has been described in detail for the purpose of illustration, but it is understood that such detail is solely for that purpose and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention, which is defined by the following claims.

What is claimed is:

1. A method of manufacturing silica comprising the steps of:

a) delivering a liquid siloxane feedstock in the liquid form to a conversion site;

b) atomizing said liquid siloxane feedstock proximate the conversion site by delivering the siloxane feedstock with a gas comprising oxygen;

c) converting said atomized siloxane feedstock into silica.

2. A method as claimed in claim 1, wherein said siloxane is octamethylcyclotetrasiloxane.

3. A method as claimed in claim 1, wherein said atomizing gas further comprises nitrogen.

4. A method as claimed in claim 3, wherein said atomizing gas consists essentially of oxygen and nitrogen.

5. A method as claimed in claim 4, wherein said atomizing gas contains at least about 50% oxygen by volume.

6. A method as claimed in claim 5, said method further comprising the step of doping said silica with at least one member of a group consisting of P_2O_5 or a metal oxide having a metallic component selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the Periodic Table of Elements.

7. A method of manufacturing a silica preform comprising the steps of:

a) delivering a liquid siloxane feedstock in the liquid form to a conversion site;

b) atomizing said liquid siloxane feedstock proximate the conversion site by delivering the siloxane feedstock with a gas comprising oxygen;

c) converting said atomized siloxane feedstock into silica.

8. A method as claimed in claim 7, wherein said siloxane is octamethylcyclotetrasiloxane.

9. A method as claimed in claim 7, wherein said atomizing gas further comprises nitrogen.

10. A method as claimed in claim 9, wherein said atomizing gas consists essentially of oxygen and nitrogen.

11. A method as claimed in claim 10, wherein said atomizing gas contains at least about 50% oxygen by volume.

12. A method as claimed in claim 11, said method further comprising the step of doping said silica preform with at least one member of a group consisting of P_2O_5 and a metal oxide having a metallic component selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the Periodic Table of Elements.

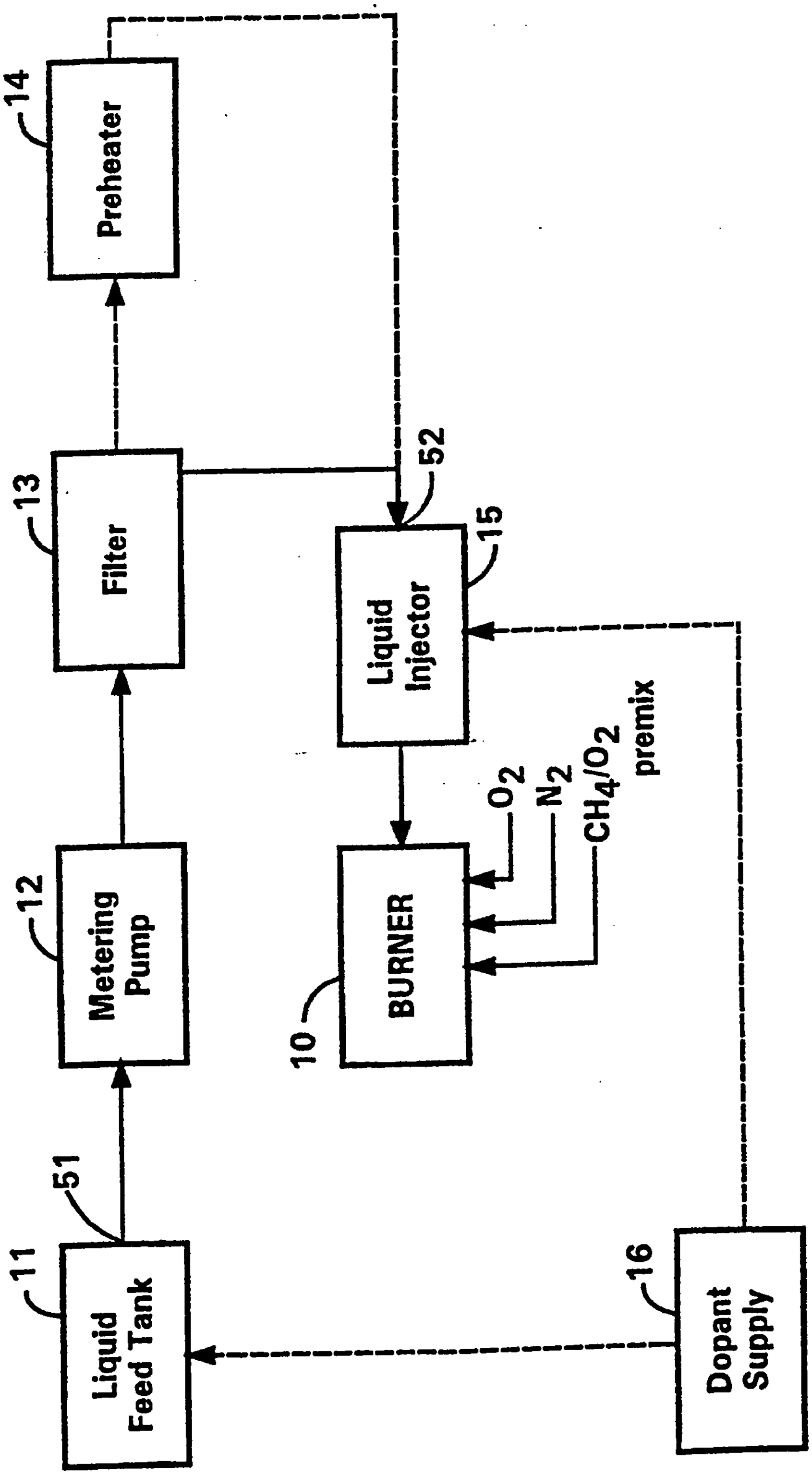

Liquid Feed Tank
11
51
Metering Pump
12
Filter
13
Preheater
14
Liquid Injector
15
52
BURNER
10
O_2
N_2
CH_4/O_2 premix
Dopant Supply
16

FIG. 1

FIG. 2

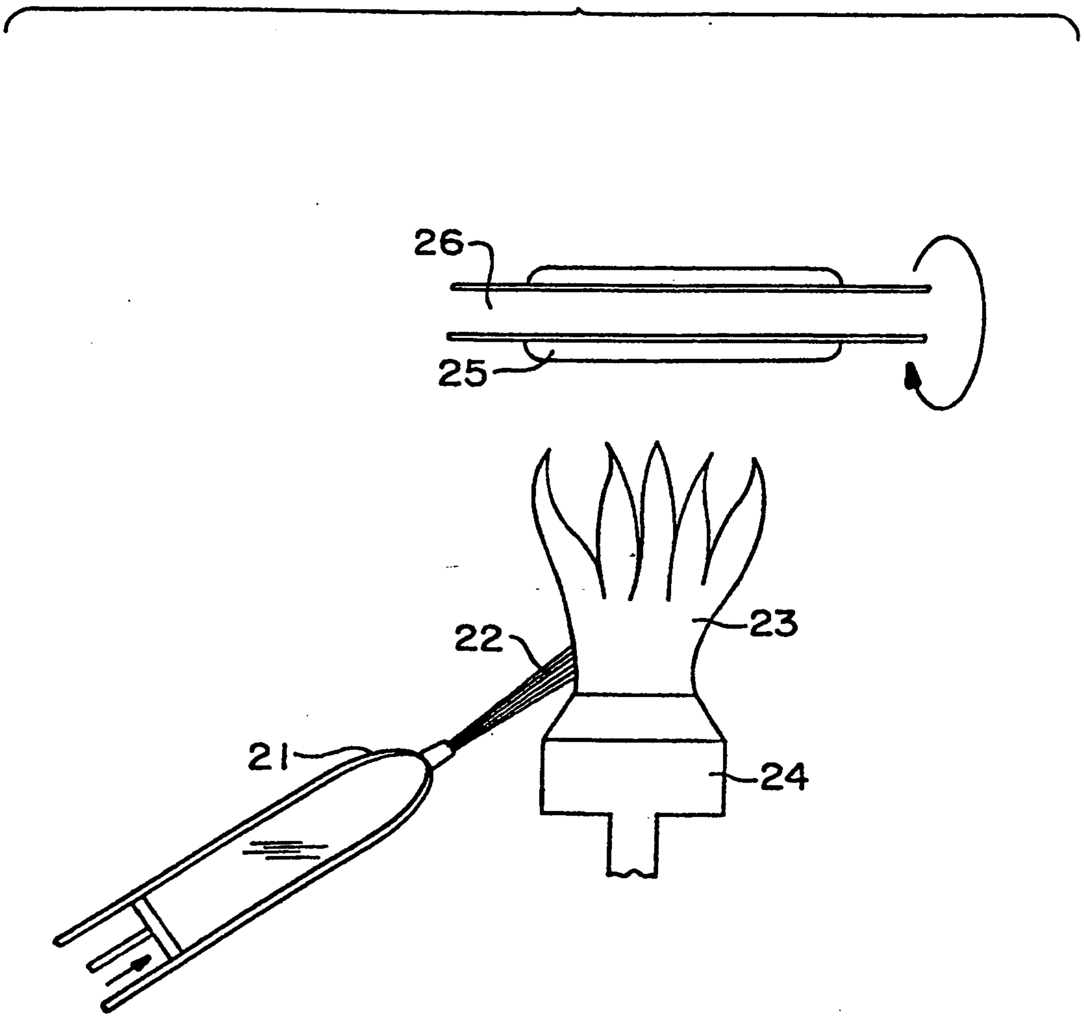


FIG. 3

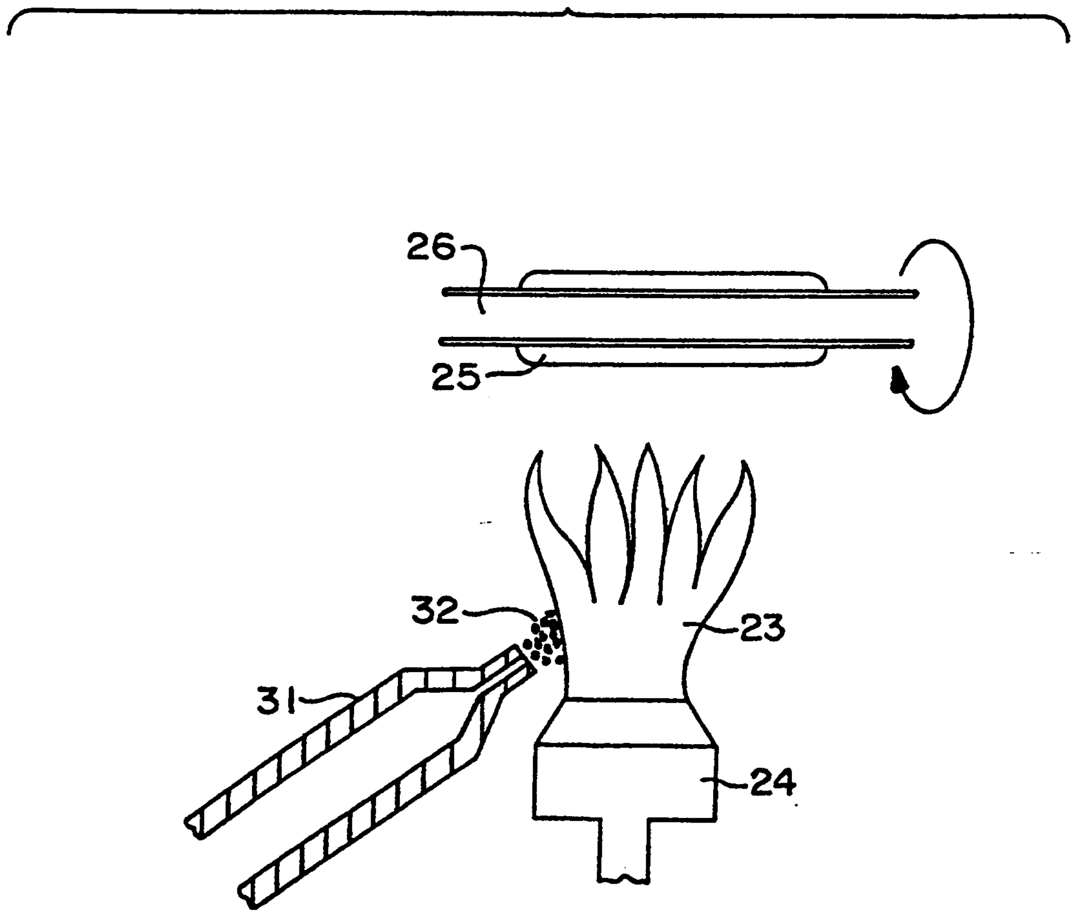
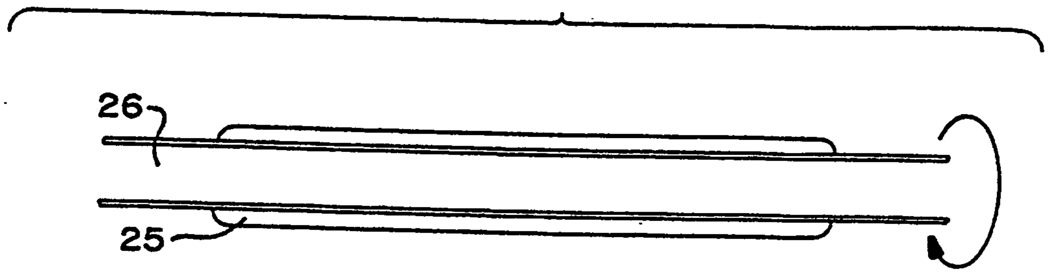
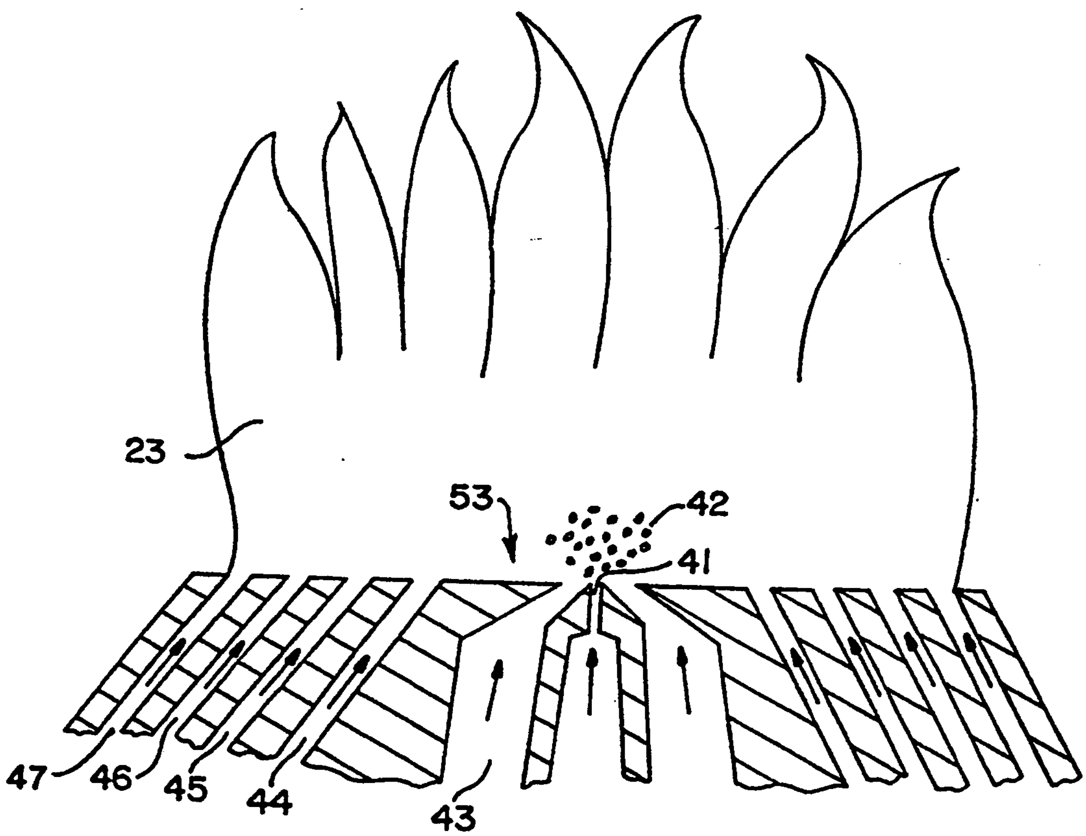


FIG. 4





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INTERNATIONAL SEARCH REPORT

Interr. ıal Application No
PCT/US 98/14060

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03B37/014 C03B19/14 C03B19/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 22553 A (CORNING INC.) 26 June 1997 cited in the application	1-12
Y	see page 16, line 26 - page 17, line 8; claims 1-23; figures 1-4	1-12
Y	EP 0 463 783 A (AT&T CO.) 2 January 1992 see column 5, line 4 - line 17; claims 1-10; figure 3	1-12
A	PATENT ABSTRACTS OF JAPAN vol. 4, no. 7 (C-70), 19 January 1980 & JP 54 142317 A (HITACHI SEISAKUSHO CO. LTD.), 6 November 1979 see abstract	1-12
A	US 4 597 983 A (R.KÜHNE ET AL.) 1 July 1986 see the whole document	1-12

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
9 October 1998	20/10/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Stroud, J

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